MODIFICATION OF HYDROPHOBIC SORBENTS BY COBALT CHLORIDE IN ORDER TO CONCENTRATE LOW MOLECULAR POLAR ORGANIC SUBSTANCES FROM THE AIR FOR SUBSEQUENT GAS CHROMATOGRAPHIC DETERMINATION

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Abstract

The article presents a new method of modification of hydrophobic sorbents. To improve sorption pre-concentration of polar organic compounds in the air analysis, these sorbents are coated with cobalt chloride. This modification increases retention volume of lower alcohols by 5-10 fold as compared to that of unmodified sorbents and solves the problem of gas-chromatographic determination at 1-2 ppb (micrograms / m3) by using the most common flame ionization detector. It should be noted that the modification of hydrophobic sorbents by cobalt chloride has little influence on their porosimetry parameters (specific surface area, proportions of meso- and micropores) and modified sorbents are capable of retaining hydrophobic nonpolar and weakly polar analytes as well as original unmodified sorbents. Thus, a fairly simple procedure leads to a large positive effect.

Keywords: Cobalt chloride; Air analysis; Pre-concentration; Sorbents; Surface-layer polytetrafluoroethylene (PTFE); Volatile organic compounds

Introduction

Determination of organic compounds in the air at the maximum permissive level and at background concentrations, usually includes a step of pre-concentration. Low molecular weight organic compounds, which are discussed in the article, are usually present in the air in their vaporized state. The main methods of concentrating vapors of volatile organic compounds (VOCs) are cryogenic concentration [1-3], solvent extraction, performed in the impinger [4] and denudors [5-6]; active [7-8] and passive [8-9] sorption of substances by sorbents contained in cartridges or tubes, as well as solid-phase microextraction (SPME) [10-11].

SPME and passive sampling are more suitable for prolonged atmospheric air control, rather than for monitoring the concentration of VOC in real time, because of their inherent slow mass transfer. Solvent extraction suggests the use of liquid analysis methods and it is not suitable for determination of readily volatile substances such as methanol. A serious problem of cryogenic VOC pre-concentration is the interfering effect of moisture that condenses in the trap. Active sampling on solid sorbents (dynamic sorption) is the most common and effective method

of low molecular weight VOCs pre-concentration in the air analysis [7, 8, 12, 13]. This is done by passing the analyzed air sample through a tube filled with sorbent. The absorbed VOCs are then desorbed by heating into a flow of carrier gas and transported to a gas chromatograph [13,14].

The greatest difficulties arise in the sorption pre-concentration of low molecular weight polar VOCs, such as methanol. All the known sorbents including activated carbon, can poorly retain similar substances at room temperature, and do not allow to reach the concentration factor exceeding 10^2. To solve this problem, we proposed high efficiency surface-layered sorbents based on nonporous salts of transition and alkaline earth metals exhibiting a high sorption affinity for lower alcohols and ketones [16]. However, these sorbents cannot provide retention of non-polar substances. According to the literature [16], these salts have a high solubility not only in water, but also in polar organic solvents. For this reason we can assume that these salts can be easily applied not only on hydrophilic, but also on hydrophobic sorbents. In particular, non-polar polymeric sorbents, which are widely used for sorption pre-concentration of organic vapors in the air analysis, can be used for this purpose [17].

The aim of this study was to evaluate the possibility of modifying the hydrophobic polymer sorbents by sorption-active, non-porous salts (SANS) and to assess their sorption properties with regard to retention of polar and non-polar volatile organic compounds.

Experimental part

Reagents and preparation of solutions and model gas mixture

All the chemicals used in this work were of analytical reagent grade (Vekton Co. Ltd, St. Petersburg, Russia). Solutions of organic substances were prepared by a volume-volume methodology. Aliquots of analytes were collected using a measuring pipette, administered into a volumetric flask, wherein the level was brought to a flask label by addition of the required liquid (water, petrolatum oil). If necessary solutions thus prepared were diluted by pure liquid.

Sorbents

The study involved modification of various micro-, meso- and macroporous hydrophobic sorbents. We used microporous bitch activated charcoal (BAC), synthesized from wood (30/50 mesh) [18]; mesoporous nonpolar polymeric sorbent Porapack QS (50/80 mesh) («Shrompack», EU); mesoporous polymer sorbent Polysorb-1 (0.25 – 0.5 mm) (Vekton Co. Ltd, St.Petersburg, Russia) – an analogue of porapack Q; macroporous polymeric sorbent Tenax GR (35/60 mesh) (Supelco, Inc); agglomerate of multi-wall carbon nanotubes - baytubes C150P (0.1 - 1 mm)

(Bayer Material Science AG, Germany), the carrier for the gas-liquid chromatography — Chromaton N-AW.

Modification of sorbents

In the process of hydrophobic sorbents modification, the calculated 0.25 g weighted quantity of cobalt chloride dehydrated by heating, was dissolved in 5 ml of polar anhydrous ethanol and mixed with 0.5 g weighted quantity of sorbent by constant stirring. The selection of ethanol for applying cobalt chloride on hydrophobic sorbents is based on the fact that this salt is poorly soluble in non-polar solvents, and water can not be used because it does not wet these sorbents. In Chromaton modification we used water solution of $CoCl_2$. The obtained mixture of the sorbent with a solution of cobalt chloride was evaporated over hot plate to loose state, then it was transferred into a drying oven and dried to constant weight at a temperature of 220 ^{0}C. The amount of coating salt was calculated via the weight increase of the sorbent, after it was riddled for separation of non coating salt. The proportion of non-separated salt equals 20–30% of the total amount of salt. The obtained sorbent was then filled in a tube with 3 mm inner diameter and a length of 7 cm.

Preparation of model gas mixture

The study of sorption properties of modified sorbents was carried out using the same model gas mixtures with known concentrations of test substances as for original sorbents. Model gas mixtures (MGM) having concentration with an order of magnitude of some mg/m^3 were prepared in accord with the standard methodology by barbotage of carrier gas through liquid solutions having sufficiently big volume (over 1 L) and a given concentration of analytes C_0. Concentration of analytes in MGM C_G is given by equation:

$C_G = C_0/K$

where K stands for distribution coefficient in gas — liquid system [19]. Solutions based on water and ethylene-glycol were used for obtaining gas mixtures of polar substances (alcohols, ketones), and paraffinic oil was used for poorly water-soluble non-polar substances (hexane, chloroform). Control concentration measurements of analytes in the generated MGM before and after experiments in all of the cases showed up only insignificant difference, thereby giving evidence of virtually constant concentration of analytes.

Evaluation of sorption properties of sorbents

A flow of the model gas mixture of tested VOC was directed to the sorption tube for concentration, and an effluent gas flow coming out of the sorption tube was directed into the dispensing loop (1 cm^3) of heated sampling valve. This valve was used for periodical withdrawal of the gas-phase samples and their injection into the gas chromatograph to determine the concentration of tested VOC's. On the obtained chromatograms we measured the heights of the peaks of analytes (h) and then compared them to the heights of the peaks obtained at injecting into the chromatograph the model gas mixture, directed to the sorption tube (h_0). Within the linear dependence of the detector signal on the analyte concentration, the value h/h_0 is equal to the value c/c_0, where c and c_0 are analyte concentrations at the outlet of the sorption tube and the inlet, respectively. We plotted output curves of tested VOCs retention as dependencies of c/c_0 on V, where V is the volume of gas passed through the tube. From these curves we determined the retention volume (V_R). The retention volume was taken equal to the volume of model gas mixture transmitted through the sorption tube, for which the following condition is satisfied: $c/c_0 = 0.5$.

Instruments

Determination of VOCs was carried out using a gas chromatograph "Kristall 5000.2" (product of "Chromatec", Russia) equipped with a flame ionization detector and a capillary tube DB-1 (60 mx 0.53 mm x 3.0 μm). The surface area and porous structure of the original and modified cobalt chloride sorbents was investigated using Accelerated Surface Area and Porosimetry System ASAP 2020 MP (Micromeritics Instrument Corp.). This system allows to analyze the size distribution of not only mesopores, but also of micropores in the range of 0.35 nm to 2 nm. Nitrogen was used as the carrier gas.

Results and discussion

The laws of VOCs retention from the gas phase by sorbents modified with cobalt chloride

Previously [15], we have found that many completely dehydrated salts of transition and alkaline earth metals have the property of strong retention of polar VOC vapors. The most probable mechanism of this retention is the ion-dipole interaction between the VOCs molecules and nodes of the salts crystal lattice. A detailed study showed that $Mg(ClO_4)_2$ provides the strongest retention of methanol vapor and acetone. However, this salt completely loses water of crystallization at temperatures above 250 ^{0}C, which is not compatible with the use of many hydrophobic and, in particular, polymeric sorbents. For this reason, we have chosen $CoCl_2$ as SANS, which although ranking 30-50% below magnesium perchlorate in sorption capacity, completely loses water of crystallization even at 150 ^{0}C.

As a result of our research it was found that the modification of hydrophobic sorbents by cobalt chloride leads to a multiple increase in methanol retention volumes (Table 1). Upon that the modification of micro- and mesoporous sorbents (active carbon, porapak, polysorb, nanotubes) has a relatively weak effect on the retention volumes of non-polar (hexane) and weakly polar (chloroform, acetone) substances. Based on this, we can assume that cobalt chloride is found primarily in the macropores of these sorbents, while meso- and micropores are not filled with salt and do not lose their ability to absorb VOCs pairs. This assumption is confirmed by the results of porosimetry studies (Table 2), from which it can be seen that the application of salt on the surface of mesoporous sorbents has a relatively weak effect on the surface area and volume of micro- and mesopores of sorbents. The situation is somewhat different in the case of macroporous Tenax (Table 1). Modification of this sorbent leads to a significant decrease in parameters of nonpolar and low polarity VOCs (hexane, chloroform). It can be easily explained by the filling of pores with salt which absorbs methanol and acetone, but does not absorb weakly polar chloroform and benzene.

Table 1 Specific volumes of retention (V_R) at 20 ^{0}C for VOCs vapor for original and modified (*) by cobalt chloride constituting 20% mass of the hydrophobic sorbent

Sorbent	V_R, l/g			
	methanol	acetone	chloroform	hexane
Activated carbon	9.3	38	37	105
Activated carbon *	48	26	28	78
Porapak QS	0.7	10.2	14.6	53
Porapak QS*	4.7	8.5	12.7	41
Polysorb-1	0.3	10.9	18.8	27.9
Polysorb-1	5.6	9.9	15.3	23.6
Nanotubes	0.7	4.6	12.4	36
Nanotubes*(10 %)	4.9	5.6	7.3	21
Tenax GT	<0.2	2.2	7.1	14.8
Tenax GT*	5.2	4.6	3.0	4.2

Table 2. Specific surface area (S_{sp}) and specific volume (V_{sp}) of the pores less than 250 nm for the original and modified (*) by cobalt chloride sorbents

Sorbent	S_{sp}, m^2/g	V_{sp}, cm^3/g
Porapak QS	510	0.76
Porapak QS* (20 %)	413	0.57
Nanotubes	197	1.35
Nanotubes* (10 %)	137	0.95

Record high volumes of methanol retention were observed for activated carbon modified by $CoCl_2$. As an illustration, Figure 1 shows output curves of methanol vapor retention from the air-based model gas mixture for regular activated carbon and the one modified by cobalt chloride (20 mass %).

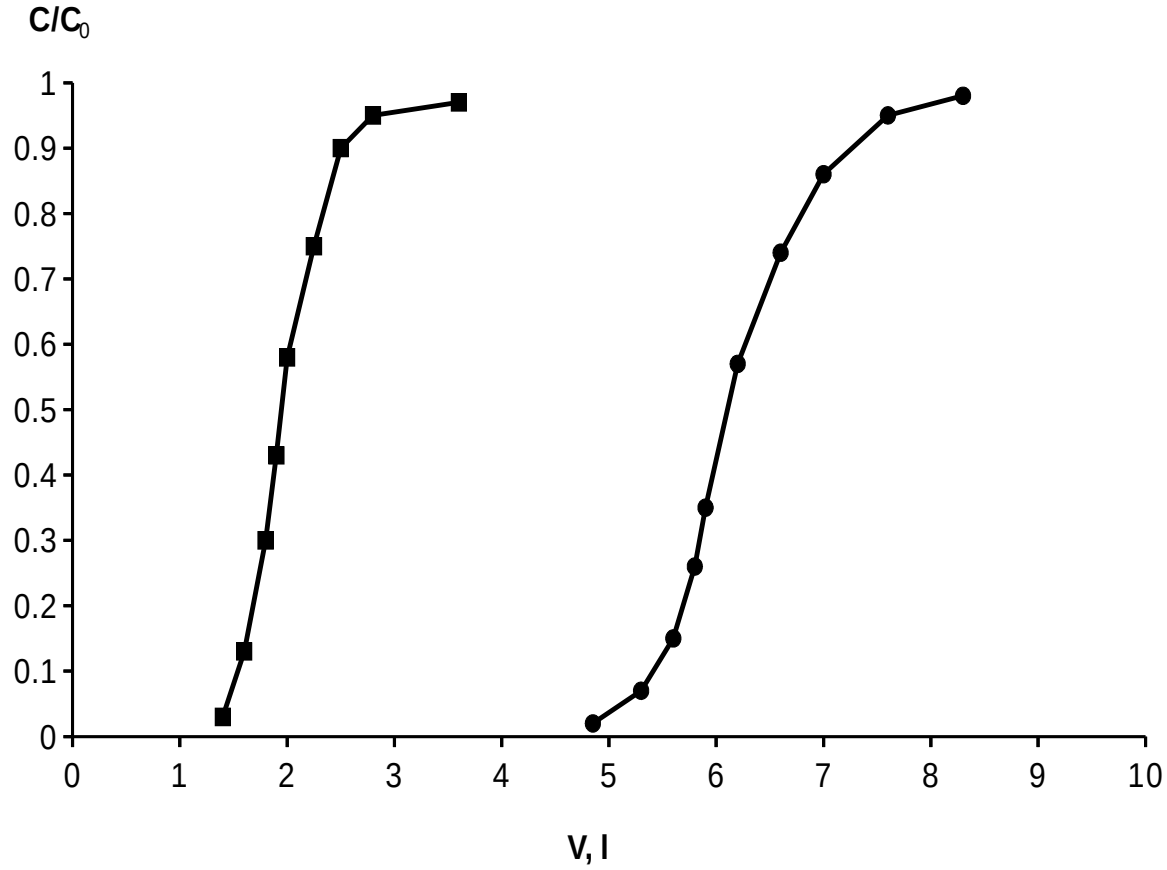
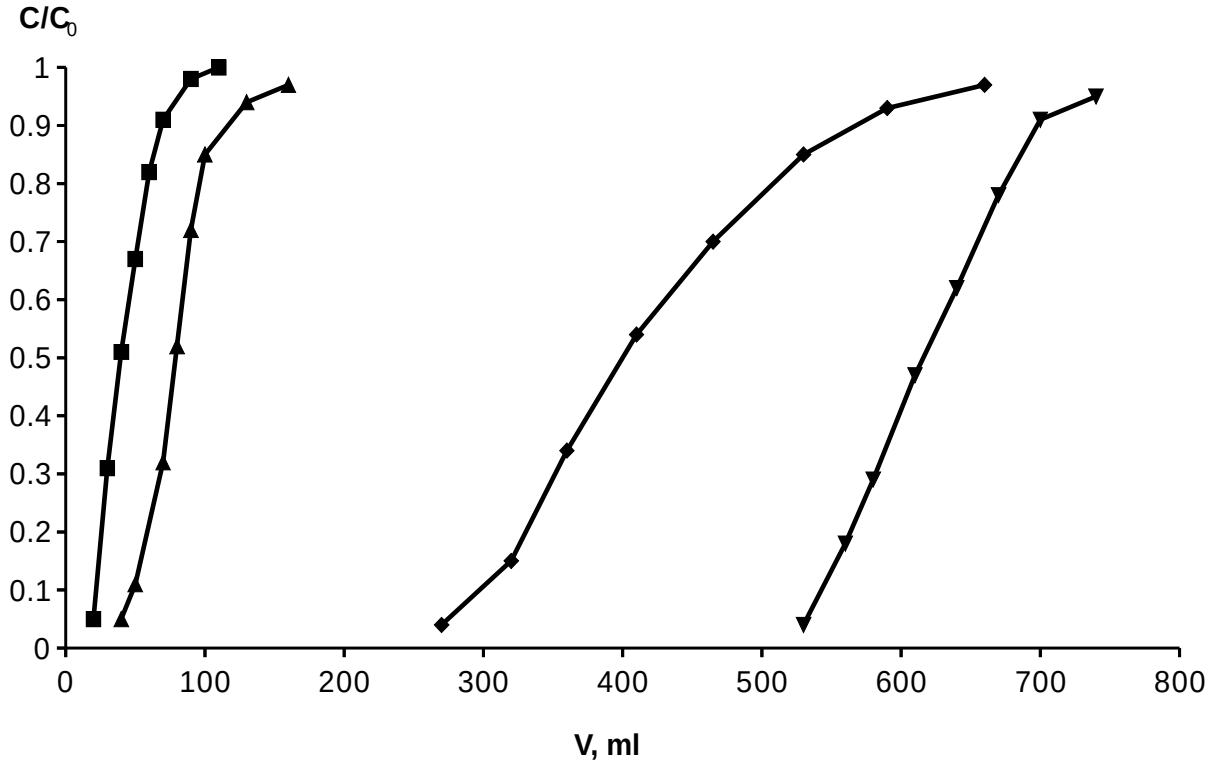


Fig. 1. Output curves of methanol vapors retention from the 250 mL / min model gas mixture flow in 7.0 x 0.3 cm tubes, filled with unmodified (1) and 20% modified by $CoCl_2$ (2) activated carbon with 0.5 – 1.0 mm particle size.

Elimination of the negative influence of water vapor on the VOC sorption pre-concentration

Sorption activity of the known sorbents, including those discussed here, is significantly reduced in the presence of water vapor. There exist 4 basic methods of removing water vapor from the analyzed flow of air containing VOC [20,21]: sorption by hydrophilic sorbent (silica gel, molecular sieves, aluminum oxide); sorption of hygroscopic salts ($Mg(ClO_4)_2$, Askarite, K_2CO_3, $CaSO_4$, $Ba(ClO_4)_2$, Na_2SO_4); cryogenic trapping and removal of water vapor by the membranes produced from ion- exchange material. A limiting factor of the most water vapor removal methods is the retention of strongly polar organic compounds such as lower alcohols, apart from water. To solve this problem, we have proposed the drying agent based on potassium fluoride which selectively absorbs water vapor and does not retain polar organic compounds. In addition to the above, potassium fluoride greatly exceeds potassium carbonate, previously used for this purpose, by its water retaining capacity[15].

Using KF –based draying agent, regardless of the nature of the sorbent in sorption tube allows us to increase the volumes to the slip of methanol from moist air. Fig.2 shows output curves of methanol retention from the air saturated with water vapor in tubes filled with unmodified (1, 2) and modified by 10% $CoCl_2$ (3, 4) nanotubes with the use of KF-based drying agent (2, 4) and without it (1, 3).



ig. 2. Output curves of methanol retention from a flow of air saturated with water vapor (W = 30 ml / min) in 7.0 x 0.3 cm tubes filled with unmodified (1), (2) and nanotubes modified by 10% $CoCl_2$ (3),(4) with the use of KF-based drying agent (2), (4) and without it (1),(3).

Along with the increase in analyte retention parameters, analyzed air pre-dehydration eliminates the interfering effect of water vapor on the thermal desorption step, which manifests itself in broadening of analyte peaks and the repeatability errors of the results in comparison with the dry air analysis.

Gas chromatographic determination of VOCs in the air with sorption pre-concentration on sorbents modified by cobalt chloride.

Despite the fact that activated carbon has the best retention volumes, it's use cause difficulties in thermal desorption of VOCs with boiling points above 70 ^{0}C [1]. For VOCs with

boiling points in the range from 30 to 200 ^{0}C, which make up more than 90% of air pollutants, more attractive in terms of sorption pre-concentration are hydrophobic polymeric sorbents with high surface area. Therefore, for sorption pre-concentration we used porapak QS, modified by 20% dehydrated $CoCl_2$.

I n sorption pre-concentration step, which in this case coincides with the stage of sampling, the flow of analyzed air is passed through sorption tubes connected-in-series by the pump at a rate of 200 ml / min (see Fig. 3.a). The first glass tube (70 x 3) mm is filled with KF-based dehydrating agent which coats the surface of the gas chromatographic diatomite support Chromaton N (NAW) with the particle size of 0.5 - 1.0 mm in the amount of 30 mass% . The second glass tube (115 x 3.5) mm is filled with modified porapak QS. After a certain volume of analyzed air passes through the pump, it is turned off, the second sorption tube is disconnected, sealed, and placed in the container in order to avoid losses of selected analytes, and then transported to the laboratory. The volume of the air sample should be less than the volume before the slip of the least retained analyte, in this case methanol.

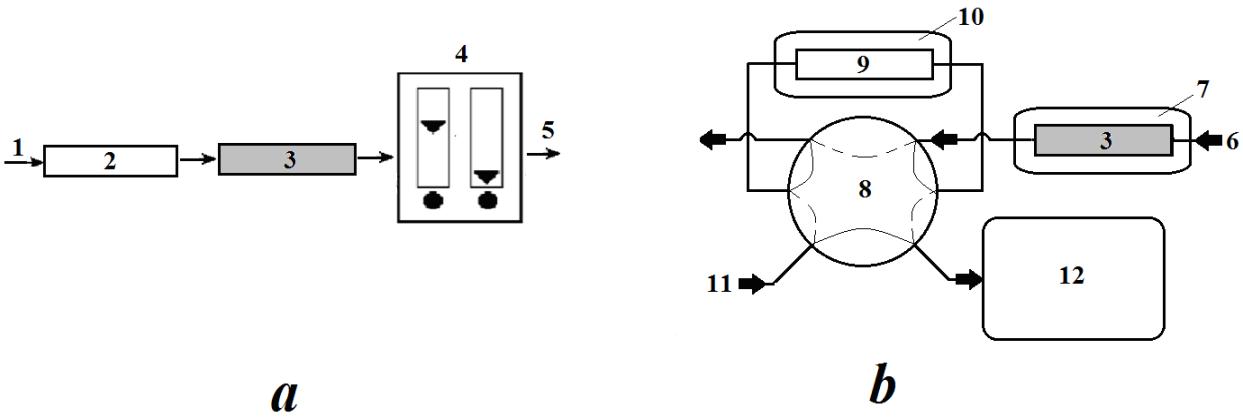


Fig. 3. Scheme of gas chromatographic analysis with sorption pre-concentration: (a) – sorption pre-concentration stage; (b) – thermal desorption and gas chromatographic analysis stage. (1),(5) – inlet and outlet of air flow; (2) – tube filled with dehydrating agent; (3) – sorption tube; (4) – pump; (6),(11) – inlets of carrier gas flow; (7) – heater; (8) – samplig valve; (9) – sorption trap; (10) – a Peltier element; (12) – gas chromatograph.

Gas chromatographic analysis was performed using a two-stage version [22] of the thermal desorption (see Fig. 3 b). At the first stage the gas valve 8 is in the position indicated in Fig.3 by solid lines. The sorption tube 3 is heated to 190 ^{0}C for 5 minutes, and during this time period desorbing analytes are transported from the tube in a flow of carrier gas with a flow rate of 6 ml / min to sorption trap 9, cooled by the Peltier element to + 1 ^{0}C. The trap consists of a glass tube (50 x 2.5) mm packed with unmodified porapak QS 80/100 mesh particle size. The results of preliminary studies showed that under predetermined conditions the trap provides

almost complete (greater than 97%) extraction of analytes from 50 mL of air. At the second stage sorption trap is almost instantaneously heated to 190 ^{0}C, gas valve is turned to the position indicated in Fig. 3b by the dashed lines and thermal desorbed analytes enter the gas chromatograph in a flow of carrier gas. The chromatogram obtained in the analysis of model gas mixture saturated with water vapor using the scheme described above is shown in Fig. 4. The chloroform peak in the chromatogram is significantly less than the peaks of other components. This is due to the differences in sensitivity of FID to mixture components.

The selected thermal desorption conditions provide ensure quantitative extraction of analytes. This is indicated by the results of the two-stage desorption. The areas of analyte peaks appearing on the chromatograms obtained during second desorption do not exceed (1-3)% of the peak area of the same analytes that appear after first thermal desorption. Provided complete extraction of analytes at all stages of sorption pre-concentration, the detection limits of analytes in the air sample C_{min} can be calculated by the approximation formula:

$$C_{min} \approx C_{min}^{0}(V_{sam}/2V_{trap}) \qquad (1)$$

C_{min}^{0}- detection limit of analytes without pre-concentration; V_{sam} - volume of analysed air passed through the sorption tube used in the first stage of sorption pre-concentration; V_{trap} - volume of sorption trap used in a second stage of sorption pre-concentration. The factor 2 in the denominator of (1) takes into account the experimental fact that, under properly selected conditions, thermal desorption volume of carrier gas required for quantitative desorption of analytes from tube containing sorbent, does not exceed double value of the volume of the tube. Table. 3 shows the estimated values of the detection limits of VOC in the implementation of two-stage sorption pre-concentration, using identical tubes (115 x 3.5) mm with conventional porapak QS and the same sorbent modified by 20% $CoCl_2$ on the first stage.

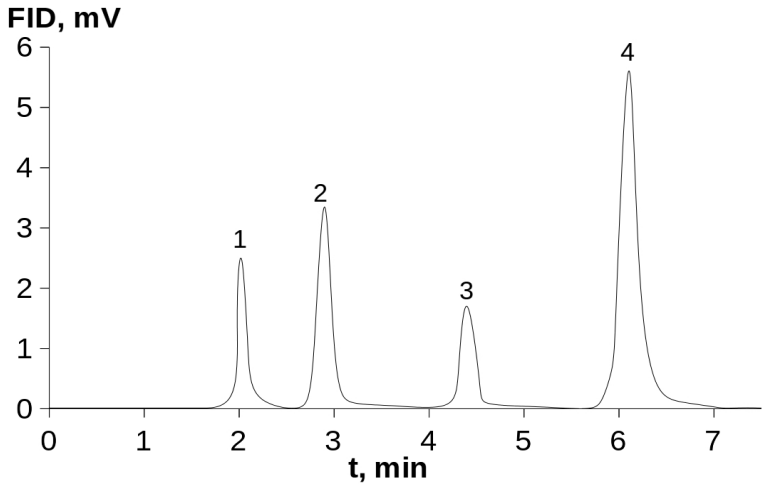


Fig. 4. Chromatogram obtained from the analysis of the model gas mixture with the analyte pre-concentration of 50 μg /m^3; (1) – methanol, (2) – acetone, (3) – chloroform, (4) – benzene.

Table 3. Estimated values of detection limits of gas chromatographic detection of VOCs in moist air for sorption pre-concentration on porapak QS: (1) – normal sorbent; (2) – sorbent modified by 20%. $CoCl_2$.

Component	The detection limit, μg / m^3	
	1	2
Methanol	10	1
Ethanol	5	1
Acetone	2	2
Chloroform	2	3
Benzene	1	2

Thus, as can be seen from Table. 3, coating the surface of porapak by $CoCl_2$ allows to lower detection limit of polar VOCs such as methanol and ethanol for several times, while for low-polarity and nonpolar VOCs this value shows no significant changes.

Conclusion

We propose simple method for modification of hydrophobic sorbents to increase their sorption capacity of the low molecular weight polar organic compounds from the gas phase. It

has been established that the application of 10 – 20% of cobalt chloride (II) of sorbent mass results in the increase of sorption parameters of alcohols 5 – 10 times. Upon that, the application of salt has little effect on the retention volumes of nonpolar and weakly polar components. The negative effect of water vapor can be eliminated by its pre-selective sorption with KF-based dehydrating agent.

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REFERENCES

[1] K. Demeestere, J.Dewulf, B. De Witt, H. Van Langenhove, J.Chromatogr. A 1153 (2007) 130.

[2] L.-L. Hsieh, C.-C.Chang, U. Sree, J.-G.Lo, Water Air Soil Pollut.170 (2006) 107.

[3] N. Oshiai, S. Daishima, D. B. Cardin, J. Environ. Monit. 5 (2003) 997.

[4] M. Michulec, W. Wardencki, M. Partyka, J. Namiesnik, Crit. Rev. Anal. Chem. 76 (2004) 3841

[5] L. N. Moskvin, T. G. Nikitina, J. Anal. Chem. 59 (2004) 2.

[6] A. Kloskowski, M. Pilarczyk, J. Namiesnik, Crit. Rev. Anal. Chem. 32 (2002) 301.

[7] E. Woolfenden, J. Chromatogr. A 1217 (2010) 2674.

[8] M. R. Ras, F. Borrull, R. M. Marce, Trend Anal. Chem. 28 (2009) 347.

[9] T. Gorecki, J. Namiesnik, Trend Anal. Chem. 21 (2002) 276.

[10] V. Larroque, V. Desauziers, P. Mocho, J. Cromatogr. A 1124 (2006) 106.

[11] M. Hippelein, Chemosphere 65 (2006) 271.

[12] K. Dettmer, W. Engewald, Chromatography 57 (2003) 339.

[13] J. Namiesnik, B. Zygmunt, Chromatography 56 (2002) 9.

[14] N. Ramirez, A. Cuadras, E. Rovira, F. Borrull, R.M. Marce, Talanta, 82 (2010) 719.

[15] O.V. Rodinkov, G.A. Zhuravlyova, A.A. Maslyakova, M.V. Petrova, L.N. Moskvin, J. Anal. Chem. 69 (2014) 347.

[16] W. Linke, A. Seidell, Solubilities of inorganic and metal-organic compounds, 4th ed. Washington, Amer. Chem. Soc. 1965.

[17] K. Dettmer, W. Engewald, Anal. Bioanal. Chem. 373 (2002) 490.

[18] S. Matysik, O. Herbarth, A. Muller, Chemosphere 76 (2009) 114.

[19] B.V. Ioffe, A.G. Vitenberg, Head Space Analysis and Related Methods in Gas Chromatography. Wiley. N.Y. 1984.

[20] W. Janicki, L. Wolska, W. Wardencki, J. Namiesnik. 1993. J. Chromatography A 654 (1993) 279.

[21] C.M. Karbiwnyk, C.S. Mills, D. Helmig, J. W. Birks. J. Chromatogr. A. 958 (2002) 219.

[22] S.M. Choa, Y.J. Kima, G.S. Heob, S.-M. Shin, Sensors and Actuators B. 117 (2006) 50.